FILM FORMING AND MECHANICAL LUBRICANT COMBINATION

RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application 60/451,871 filed March 4, 2003, the disclosure of which is incorporated herein for all purposes.

FIELD OF THE INVENTION

[0002] The present invention relates to lubricants having a film-forming component, a suspension agent, and a mechanical lubricant, and use of the lubricants for example in oilfield applications including use in drilling fluids workover and completion fluids.

BACKGROUND OF THE INVENTION

[0003] Lubricant compositions are materials that can be introduced between opposed solid surfaces, e.g. the surfaces of machine parts, in order to prevent these surfaces from contacting each other and to facilitate any relative motion between them as far as necessary. As a consequence, such lubricant compositions normally need to have hydrodynamic properties, i.e. the capacity of building up an internal pressure which is sufficient to balance the load on the opposed surfaces, and further friction-reducing and wear-reducing properties.

[0004] Many lubricant compositions have the form of oils and greases and can be used for a wide variety of applications. Lubricant oils may be based on petroleum derivatives, animal or vegetable oils or on synthetic materials such as polyalkylene glycols, dibasic esters, phosphate esters, silicones, silicate esters and the like. Lubricant greases are combinations of such oils with thickening agents such as *e.g.* metal soaps, modified clays, fine silicas and the like, and/or fillers such as e.g. asbestos, graphite, metal carbonates, hydroxides, oxides, phosphates, sulfides and the like. Moreover, lubricant oils and greases may contain special additives, e.g. to resist oxidation and corrosion and to improve such properties as adhesion, film strength and resistance to water wash out.

[0005] Lubricants of the type described herein at particular useful when incorporated with or used in conjunction with drilling muds or fluids. United States Patent 4, 230,586 relates to aqueous well-drilling fluids containing additives comprising colloidal disperse systems and emulsifiers. Such additives provide lubricity to the drilling fluids and thus allow rotary drilling operations to be carried out at reduced torque and drag (vertical movement). Methods of carrying out drilling operations

using these drilling fluids are also within the scope of this reference. United States Patent 4,301,016 provides a method for drilling a borehole wherein a drilling fluid comprises an aqueous composition which contains an effective amount of an emulsion polymerized latex comprised of an interpolymer of an olefinically unsaturated carboxylic acid monomer and at least one other, non-carboxylated polymerizable monomer.

[0006] The primary functions of a drilling fluid mud are: to carry chips and cuttings produced by drilling to the surface; to lubricate and cool the drill bit and drill string; to form a filter cake which obstructs filtrate invasion in the formation; to maintain the walls of the borehole; to control formation pressures and prevent lost returns; to suspend cuttings during rig shutdowns; and to protect the formation for later successful completion and shutdown. Drilling muds or fluid in oil wells are normally pumped continuously down the drill stem, through apertures in the drill bit and are then forced up to the surface through the annular space between the drill stem and the side of the hole, carrying the rock cuttings in suspension. At the surface the cuttings are separated from the drilling mud and the latter is then recycled. Prior to cementing the mud is replaced by a Spacer Fluid which transports loose particles from the hole and leaves a clean, water-wet surface to provide a good cement bond.

[0007] Certain rocks cause particular problems during drilling or excavation, due to their tendency to disintegrate in the drilling fluid to form fines which are very difficult to separate from the fluid and rapidly build up in the recycle stream causing increasing viscosity. Chief among the problem rocks is shale which generally disintegrates in the presence of water. An acceptable drilling fluid or mud needs to have a viscosity which is sufficiently low under conditions of shear to flow readily, but it also has to possess solid suspending properties. To achieve these conflicting requirements a thixotropic fluid is usually required. Moreover it must not cause excessive breakdown of rocks such as shale. If it is to be useful for deep drilling, the fluid must be thermally stable, and it is important that excessive loss of fluid into the formation should be avoided. These requirements have been achieved by using either oil or an oil-in-water emulsion as the drilling fluid. The oil coats particles of shale and protects them from contact with water, thereby inhibiting their disintegration. However this in turn creates an environmental problem, especially in offshore drilling operations, when the rock cuttings are discarded. To avoid serious pollution the oil must be cleaned from the cuttings, before they can be dumped. It is difficult and expensive to reduce the oil contamination to currently permitted levels, but even these small amounts of residual oil are ecologically undesirable, and there

is pressure to replace oil based drilling fluids altogether. Oil-based muds/fluids also give rise to a fire hazard.

[0008] Prior art oil-based drilling muds and lubricants have contained minor proportions of surfactants as emulsifying agents for the oil or as dispersants for sludge. The surfactants have typically been present essentially as monolayers surrounding colloidal size droplets or particles of oil or dispersed solid. The protection of shale in drilling muds has been essentially due to the shale being coated with oil. The suspending properties and thixotropic character of oil based drilling mud has been provided by the interaction of the dispersed oil droplets.

[0009] However environmental pressure is increasingly compelling drilling companies to adopt water based fluids in place of oil based muds. An aqueous solutions containing polymeric suspending agents or dispersants and/or bentonite to suspend the rock cuttings is less environmentally harmful, and may be somewhat cheaper than the use of oil based muds. The solid suspending properties are provided by polymeric thickeners such as sodium carboxymethyl cellulose or methacrylates. In the case of water-based muds, the protection of the shale has been provided by the presence of polymers which encapsulate the shale particles irreversibly and are therefore consumed quantitatively when the rock is drilled. For deep drilling or for drilling through shale, such aqueous fluids are often inadequate. They have insufficient thermal stability to withstand the high temperatures of deep formations and they can cause breakdown of the shale. Their lubricity is also generally inferior to that of oil based muds. Attempts have been made to improve the performance of aqueous drilling fluids with a variety of special additives such as polymeric coating agents, and high concentrations of electrolyte to help stabilize shale. These have not succeeded in providing an aqueous fluid with adequate performance to replace oil based muds for deep drilling.

[0010] Solid particle lubricant compositions, which have particulate solids, are used in cases where the opposed surfaces are subjected to extreme pressures and work loads during use. Such particulate solid lubricants may consist of inorganic compounds having laminar crystal lattices such as crystalline graphite, molybdenum disulphide and the like, other soft inorganic compounds such as lead oxide, lime, talc, bentonite and the like, soft organic compounds such as soaps, waxes and fats, soft polymers such as poly(tetrafluoroethylene) or poly(chlorofluoroethylene) and the like, or malleable metals such as aluminium, copper, lead and the like, or fracturable metals such as zinc. These solid lubricant solids are elastic, malleable or fracturable, and they are generally soft in the

particular sense of having rather low yield limits to their mechanical properties. The particulate solid lubricants may be used as such or as dispersions in oils, even water-based vehicles.

[0011] United States Patent 4,280,915 describes a base drilling fluid which has enhanced lubricating properties in the presence of polyvalent cations comprising a mixture of (1) water; (2) finely divided inorganic solids; (3) an alkanolamide of a saturated fatty acid having 8 to 20 carbon atoms, or triglycerides thereof, and (4) an alkanolamide of an unsaturated fatty acid having 18 carbon atoms, or triglycerides thereof. The alkanol amide is a reaction product of a mono- or di-substituted amines having C1 -C10 range mono- and di-alkanol substituents, and a reactant selected from the group consisting of C8 -C20 range saturated fatty acids or triglycerides wherein at least 50% of the fatty acids are saturated. The unsaturated fatty acid, however, should not be reacted with excess amounts of alkanolamine. United States Patent 5,007,489 suggests drilling lubricants comprising a system, one component of which is an amine sulfonate prepared from a half ammonium, half isopropylamine salt of the sulfosuccinic acid ester of the oleic acid amid of isopropanol amine.

[0012] U. S. Patent 5,348,938 teaches adding oleophilic basic amine compounds to drilling fluid in amounts of up to about 10 lb/bbl.

[0013] United States Patent 4,715, 971 provides a well drilling and completion composition having a potassium salt of a copolymer of a first compound with a formula $CH_2=CR_1$-COOH wherein R_1 is selected from the group consisting of H, and an alkyl having 1 to 4 carbon atoms, and a second compound having a formula $CH_2=CH$--$COOR_2$ wherein R_2 is selected from the group consisting of an alkyl radical and a hydroxyalkyl radical wherein the alkyl and hydroxy each have 1 to 4 carbon atoms. The well drilling and completion composition of this invention also has an accelerator catalyst which includes water, KOH, lignite, sulfonated polystyrene, and a vinylsulfonate/vinylamide copolymer if the temperature of the system is above 285° F.

[0014] United States Patent 5,223,163 is directed to improved viscosity properties resulting from highly alkaline low viscosity overbased phenates comprising the overbased reaction product of a source of alkylated phenol, and a source of an alkali or alkaline earth metal containing reagent which is overbased in the presence of a dispersant composition and a carboxylic acid or its derivative.

[0015] The use of polymeric beads as a lubricant or a fluid loss additive in drilling mud is known. United States Patents 4,063,603; 4,172,031; 4,269,279; 4,384,095 and 4,427,793 describe beads of one or more crosslinked polymers, *e.g.*, polymers of styrenes, PVC/vinylacetate, vinylidene

chloride/acrylonitrile, methylmethacrylate and ethylacrylate, and styrene and divinylbenzene copolymers, that are useful in a drilling environment. United States Patent 4,063,603 describes using beads as a lubricant, wherein the beads are further aided by other lubricants, *e.g.*, vegetable oils, such that the beads are suspended in vegetable oil and circulated in the well bore mixed with the drilling mud.

[0016] United States Patent 5,792,727 describes lubricant compositions such as drilling muds and high pressure lubricants, which can be used for applications where extreme pressures and work loads are involved. The lubricant compositions are dispersions of solid particles in a supporting vehicle. The solid particles are substantially spherical particles of a hard, abrasion-resistant and fracture-resistant, thermally stable and chemically inert material. This patent teaches that suitable particles are made primarily of ceramic materials, although some materials of other nature may also be appropriate, particularly silica-based materials. Examples include particles of silica-alumina ceramics, optionally including oxides of other materials, and fused silica. This patent teaches that glass beads having a hardness of 5.5 on the Moh's scale are generally unsuitable since they have a low compressive strength, a softening point of about 730° C. and they are susceptible to attack by alkali. The solid particles are incorporated in a supporting vehicle which may be any petroleum-based, organic-based, silicone-based or even water-based vehicle, preferably lubricant oils and greases. The lubricant greases to be used as a supporting vehicle will normally be a combination of such oils with thickening agents, such as e.g. metal soaps (salts of alkaline or alkaline earth metals with monobasic or polybasic aliphatic acids, such as sodium, lithium, barium stearates, hydroxystearates, oxalates, sebacates and the like), modified clays, fine silicas and the like, and/or fillers or additives such as e.g. asbestos, graphite, metal carbonates, oxides, hydroxides, phosphates, sulphates, sulfides, and the like. Such thickening agents, fillers and additives are normally used in gelled form or in fine particulate form, as appropriate. The lubricant composition may preferably comprise about 50 to 60% by weight of particles of a hard, abrasion-resistant and fracture-resistant, thermally stable and chemically inert material, and about 40 to 50% by weight of a lubricant oil or lubricant grease.

[0017] United States Patent 5,700,767 describes a downhole well lubricant having the properties of coating metal surfaces submerged in a water based well liquid and, in response to friction between the coated metal surfaces submerged in the water based well liquid, producing a greasy water based emulsion on the metal surfaces, the lubricant consisting essentially of 20-70 pounds per barrel of a

stearate surfactant; and a liquid component being 20-50% of a filming amine; 20-80% of an activator selected from the group consisting of petroleum solvent comprising a mixture of C7-C10 saturated hydrocarbons, 1, 2, 4 trimethylbenzene and C8+ aromatics; coconut oil; terpene; xylene; toluene; benzene; mineral oil; turpentine; and mixtures thereof, and balance diluent

[0018] United States Patent 5,851,961 describes an anti-settling lubricity agent for water/oil dispersions comprising a mixture of: water;

A) an overbased non-Newtonian colloidal mixture of solid metal-containing colloidal particles, e.g., alkali or alkaline earth metal acetates, formates, carbonates, sulfides, sulfites, thiosulfides, and halides, predispersed in a dispersion medium of at least one inert organic liquid and at least one organic compound having polar substituents and hydrophobic portions which is substantially soluble in the disperse medium;

(B) a water soluble associative thickener comprising a base-neutralized carboxlated copolymer of a carboxyl-containing, ethylenically unsaturated hydrocarbon and a nonionic surfactant acrylate; and

[0019] (C) at least one carboxylic acid is selected from the group consisting of tall oil fatty acids, linoleic acid, abietic acid, linolenic acid, palmitoleic acid, oleic acid and ricinoleic acid.

[0020] What is needed is lubricant compositions containing environmentally benign components, where the composition is useful at deep pressures but which advantageously has substantially no inorganic solid material.

SUMMARY OF THE INVENTION

[0021] In a first embodiment, the inention is a lubricant composition comprising:

A) between about 40% and about 80% by volume of a film forming lubricant consisting essentially of unsaturated fatty acid(s) having between about 16 and about 26 carbon atoms and between one and three carboxylic acid moieties, or triglyceride(s) having from about 16 to about 26 carbon atoms and at least one double bond, or mixture thereof;

B) at least about 20% by weight of a suspension agent comprising:

1) a metal compound reactable with at least one carboxylic acid moiety in the unsaturated fatty acid, wherein the metal is a Group I metal, a Group II metal, or mixture thereof;

2) a film-forming amine R_1-N-$(R)_2$, where:

a) each R is independently an H or a C_2 to C_5 alkylene, and R_1 is a C_3 to C_{24} saturated or unsaturated aliphatic group or two saturated or unsaturated aliphatic groups with an oxygen therebetween, wherein the amine has between ten and thirty carbon atoms;

b) each R is independently an H, a C_2 to C_5 alkylene, or a C_1 to C_5 alkyl or alkanol, and R_1 contains between 10 and 24 carbon atoms and is a C_{10} to C_{24} mono- or poly-unsaturated hydrocarbon radical or a group R_2-O-R_3; wherein R_2 and R_3 are hydrocarbon moieties and at least one of R_2 and R_3 is a mono or poly-unsaturated hydrocarbon radical; or

c) mixtures thereof, wherein the amount of suspension agent is sufficient to provide at least a 50% overbased composition; and

C) between about 10 and about 50 pounds of a polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition, wherein said lubricant composition is blended to form a substantially homogenous composition.

[0022] In an alternate embodiment, the lubricant composition comprises:

between about 50% and about 75% by volume of tall oil fatty acids;

between 20% and about 45% by weight of the suspension agent; and

between about 10 and about 35 pounds of the polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition.

[0023] In another alternate embodiment, the lubricant composition consists essentially of:

between about 50% and 80% by volume of tall oil fatty acids;

between 20% and about 45% by weight of the suspension agent, wherein the suspension agent comprises the metal compound, and wherein the metal is a Group I metal, a Group II metal, or mixture thereof; and

between about 10 and about 35 pounds of the polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition.

[0024] In another alternate embodiment, the lubricant composition comprises:

between about 60% and about 70% by volume of unsaturated fatty acid(s) having between about 18 and about 22 carbon atoms and between one and three carboxylic acid moieties;

between 30% and about 40% by weight of the suspension agent, wherein the suspension agent comprises the metal compound, and wherein the metal is a Group I metal, a Group II metal, or mixture thereof; and

between about 15 and about 20 pounds of the polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition.

[0025] In another alternate embodiment, the lubricant composition comprises:

between about 60% and about 70% by volume of tall oil fatty acids;

between 30% and about 40% by weight of the suspension agent, wherein the suspension agent comprises a metal base compound, and wherein the metal is a Group I metal, a Group II metal, or mixture thereof; and

between about 15 and about 20 pounds of a polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition.

[0026] In another alternate embodiment, the lubricant composition comprises:

between about 60% and about 70% by volume of the unsaturated fatty acid(s) having between about 16 and about 26 carbon atoms and between one and three carboxylic acid moieties, the triglyceride(s) having from about 16 to about 26 carbon atoms and at least one double bond, or mixture thereof;

between 30% and about 40% by weight of the suspension agent, wherein the suspension agent comprises the metal compound, and wherein the metal is a Group I metal, a Group II metal, or mixture thereof; and

between about 10 and about 35 pounds of a polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition.

[0027] In another alternate embodiment, the lubricant composition consists essentially of:

between about 60% and about 75% by volume of the unsaturated fatty acid(s) having between about 18 and about 22 carbon atoms and between one and three carboxylic acid moieties;

between 30% and about 40% by weight of the suspension agent, wherein the suspension agent comprises the metal compound, and wherein the metal is a Group I metal, a Group II metal, or mixture thereof; and

between about 15 and about 20 pounds of the polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition.

[0028] In any of the above embodiments, the film forming lubricant may comprise at least 50% by weight of one or more tall oil fatty acids.

[0029] In any of the above embodiments, the suspension agent may consist essentially of a metal salt, wherein the metal is sodium, potassium, and lithium, magnesium, calcium, barium, or mixture thereof.

[0030] In any of the above embodiments, the metal ratio is beneficially between about 2 and 12.

[0031] In any of the above embodiments, the polymeric particulate advantageously consist of polymeric beads having a size between 40 mesh to 100 mesh, wherein the beads comprise a cross-linked polymer or copolymer of styrene, divinylbenzene, PVC/vinylacetate, vinylidene chloride/acrylonitrile, methylmethacrylate/ethylacrylate, or styrene/divinylbenzene.

[0032] In any of the above embodiments, the polymeric particulate advantageously consists of polymeric beads having a size between 60 mesh to 80 mesh, the beads comprising a cross-linked polymerized divinyl benzene, styrene, divinyl benzene/styrene, polystyrene crosslinked with divinyl benzene, or mixtures or combinations thereof.

[0033] In any of the above embodiments, the polymeric particulate advantageously consists of polymeric beads having a weight average particle diameter between about 220 and about 280 microns, with less than 30% by weight having a diameter less than 150 microns and less than 5% by weight having a diameter greater than about 350 microns.

[0034] In any of the above embodiments, advantageously the lubricant composition comprises less than about 2% by weight of each of: promoters useful for forming the overbased film forming lubricant/suspension agent composition; resin acids; unsaponifiables; and saturated fatty acids and their isomers. Preferably, the lubricant composition comprises less than about 5% by weight total of promoters useful for forming the overbased film forming lubricant/suspension agent composition, resin acids, unsaponifiables, and saturated fatty acids.

[0035] In any of the above embodiments, advantageously the lubricant composition comprises less than about 1% by weight of each of: promoters useful for forming the overbased film forming lubricant/suspension agent composition; resin acids; unsaponifiables; and saturated fatty acids and their isomers.

[0036] In any of the above embodiments, advantageously the lubricant composition further comprises between about 0.1% and about 5%, of inorganic particulate lubricant, for example, beads or particles of graphite, molybdenum disulphide, lead oxide, aluminum, copper, lead, zinc, glass, or ceramic. Preferably, the inorganic particulate lubricant comprises or consists essentially of graphite, molybdenum disulphide, glass, or ceramic.

[0037] In any of the above embodiments, advantageously the film forming lubricant comprises at least 50% by weight of unsaturated fatty acids having between 18 and about 20 carbon atoms.

[0038] In any of the above embodiments, advantageously the lubricant composition is substantially free of aromatics, cadmium, and lead, e.g., contains less than 500 ppm of each, preferably less than 100 ppm of each.

[0039] In any of the above embodiments, advantageously at least half of the equivalents of the suspension agent are salts or bases of Group II metals. Alternatively, at least half by weight of suspension agent is an alkaline earth metal base where the counter-ion is a hydroxyl, a carbonyl, a carbonate, or mixture thereof.

[0040] The above-described lubricants are particularly useful in treating wells during drilling or work-over operations including for example running coiled tubing. The method of lubricating a pipe in a wellbore comprises:

adding between about 0.2% and about 5%, preferably 0.5% to 4%, or 2-3% by volume of the lubricant composition of claim 1 to a treating fluid; and

circulating the fluid containing the lubricant into the well to place the lubricant at the desired depth.

[0041] The treating fluid can be an aqueous-based drilling mud or an oil-based drilling mud, as well as simply oil or brine, or any combination thereof.. The treatment amount is preferably about 2% and about 3% by volume.

[0042] In a preferred embodiment, the lubricant composition comprises:

between about 50% and about 80% by volume of a film forming lubricant consisting essentially of unsaturated fatty acid(s) having between about 18 and about 24 carbon atoms and between one and three carboxylic acid moieties;

between 20% and about 45% by weight of a suspension agent comprising a metal salt or metal base reactable with at least one carboxylic acid moiety in the unsaturated fatty acid, wherein the metal is a Group I metal, a Group II metal, or mixture thereof, wherein the amount of suspension agent is sufficient to provide at least a 50% overbased composition; and

between about 10 and about 35 pounds of a polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition, wherein the polymeric particulate consists of polymeric beads having a size between 40 mesh to 100 mesh, the beads comprising a cross-linked

polymer or copolymer of styrene, divinylbenzene, PVC/vinylacetate, vinylidene chloride/acrylonitrile, methylmethacrylate/ethylacrylate, or styrene/divinylbenzene; wherein said lubricant composition is blended to form a substantially homogenous composition.

[0043] This preferred lubricant may further comprise between 5% and 20% by weight of a film-forming amine R_1-N-$(R)_2$, where:

each R is independently an H or a C_2 to C_5 alkylene, and R_1 is a C_3 to C_{24} saturated or unsaturated aliphatic group or two saturated or unsaturated aliphatic groups with an oxygen therebetween, wherein the amine has between ten and thirty carbon atoms;

each R is independently an H, a C_2 to C_5 alkylene, or a C_1 to C_5 alkyl or alkanol, and R_1 contains between 10 and 24 carbon atoms and is a C_{10} to C_{24} mono- or poly-unsaturated hydrocarbon radical or a group R_2-O-R_3; wherein R_2 and R_3 are hydrocarbon moieties and at least one of R_2 and R_3 is a mono or poly-unsaturated hydrocarbon radical; or

mixtures thereof.

[0044] In a preferred embodiment, the lubricant composition consisting essentially of

between about 50% and about 75% by volume of a film forming lubricant consisting essentially of unsaturated fatty acid(s) having between about 18 and about 24 carbon atoms and between one and three carboxylic acid moieties;

between 20% and about 45% by weight of a suspension agent comprising a metal salt or metal base reactable with at least one carboxylic acid moiety in the unsaturated fatty acid, wherein the metal is a Group I metal, a Group II metal, or mixture thereof, wherein the amount of suspension agent is sufficient to provide at least a 50% overbased composition; and

between about 15 and about 30 pounds of a polymeric particulate that functions as a mechanical lubricant per barrel of lubricant composition, wherein the polymeric particulate consists of polymeric beads having a size between 40 mesh to 100 mesh, the beads comprising a cross-linked polymer or copolymer of styrene, divinylbenzene, PVC/vinylacetate, vinylidene chloride/acrylonitrile, methylmethacrylate/ethylacrylate, or styrene/divinylbenzene; wherein said lubricant composition is blended to form a substantially homogenous composition.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0045] The present invention is a lubricant that has the combined properties of a liquid film forming lubricant and a mechanical lubricant. The combined lubricant of the present invention includes the following three components:

a film forming liquid lubricant, e.g., one or more tall oil fatty acid compounds;

a suspension agent, e.g., an alkali metal, alkali earth metal, or metal oxide or carbonyl; and

a particulate mechanical lubricant, e.g., a polymeric solid advantageously preformed into discrete particles.

[0046] In one embodiment, the lubricant composition comprises:

between about 40% and about 80%, preferably between about 50% and about 75%, more preferably from about 60% to about 70% by volume of a film forming liquid lubricant, e.g., one or more tall oil fatty acid compounds;

between about 10% and 50% for example between about 20% and about 45%, or between about 30% and about 40% by weight, of a suspension agent, e.g., an alkali metal, alkali earth metal, or metal compound, wherein the metal ratio is at least about 1.5, for example between about 2 and 12, alternately between about 3 and 6; and

between about 10 and about 50, for example between 10 and about 35, or alternately between about 15 to about 20 pounds per barrel of lubricant of a polymeric particulate mechanical lubricant, e.g., polystyrene or polydivinylbenzenestyrene beads.

[0047] The lubricant composition can optionally contain any of the following:

promoters useful for forming the overbased film forming lubricant/suspension agent composition, so long as the amount of promotors is less than about 2% by weight, for example between 0.1% and 1.9% by weight;

between about 0 and about 2%, for example between about 0.1% and 1%, each of resin acids, unsaponifiables, and saturated fatty acids and their isomers; and

between about 0 and about 5%, for example between about 0.1% and 4%, of additional inorganic particulate lubricant material comprising graphite, molybdenum disulphide, lead oxide, lime, talc, bentonite, or particles of aluminum, copper, lead, zinc, glass, or ceramic.

[0048] In a preferred embodiment the lubricant composition is substantially free of promoters. In a preferred embodiment the lubricant composition is substantially free of resin acids, unsaponifiables, and saturated fatty acids and their isomers. In a preferred embodiment the lubricant composition is

substantially free of inorganic particulate lubricant material. In each case substantially free means less than 0.3% by weight of the component(s) in the lubricant composition. In another embodiment the lubricant composition comprises between 0.1% and 4% of inorganic particulate lubricant material selected from graphite, molybdenum disulphide, glass, or ceramic.

[0049] Each component will now be further described.

[0050] Generally, the amount of film forming liquid lubricant is between about 50 and 75 V/V%, preferably from about 60 to about 70 V/V%, based on the volume of the lubricant composition. The film forming liquid lubricant comprises or consists essentially of one or more of:

1) a fatty acid having between about 16 and about 26 carbon atoms, preferably having between about 18 and about 20 carbon atoms, and between one and three carboxylic acid moieties per molecule, preferably having one carboxylic acid moiety per molecule, and preferably having between 1 and 3 carbon-carbon double bonds; and

2) a triglyceride with the fatty acids having from about 16 to about 26 carbon atoms and at least one double bond, but no more than three double bonds for at least 90% of the fatty acids. All isomers of these are included, but straight chain groups are preferred.

[0051] In one preferred embodiment, the film forming liquid lubricant comprises at least 50% by weight of, or consists essentially of, one or more tall oil fatty acids, having for example from about 18 to about 20 carbon atoms with the majority of fatty acids having one double bond. In another embodiment, the film forming liquid lubricant comprises at least 50% by weight of, or consists essentially of, one or more of linoleic acid, abietic acid, linolenic acid, palmitoleic acid, oleic acid and ricinoleic acid. The film forming lubricant should be ecologically acceptable and accordingly in the preferred embodiment should have no aromatic constituents. Straight-chain and/or branched unsaturated, particularly olefin mono- and/or poly-unsaturated, fatty are the preferred compounds. In a preferred embodiment, the film forming liquid lubricant comprises at least 50% by weight of, or consists essentially of, one or more tall oil fatty acids, e.g., a light-yellow oily liquid which is a mixture of high molecular unsaturated organic acids such oleic, linoleic, linolenic acids and their isomers. In another preferred embodiment, the film forming liquid lubricant comprises at least 50% by weight of, or consists essentially of, one or more of linoleic acid, linolenic acid, and oleic acid. A normal sunflower oil has from 20-40 percent oleic acid and from 50-70 percent linoleic acid. In one embodiment, the film forming liquid lubricant is comprised of EZESlide™, a tall oil fatty acid compound, marketed by Sun Drilling Products, Inc.

[0052] Film forming lubricants typically are commercially available in mixtures with certain contaminants, in particular resin acids, unsaponifiables, and saturated fatty acids and their isomers. The preferred lubricant compositions are substantially free of these components. By substantially free it is meant less than 2%, preferably less than 1%, of each of the three general components. Resin acids are believed to cause undesired thickening. Unsaponifiables are a general term for organic contaminants that are typically undefined. Saturated fatty acids are used in many prior art lubricant formulations, but applicants have found that when present, they have a tendency to react with low-salinity brines to form undesirable foams.

[0053] The lubricant composition typically comprises between about 20% and about 45%, for example between about 30% and about 40% by weight, of a suspension agent. The suspension agent generally comprises or consists essentially of one or more metal compounds described infra. The metal compounds useful in making the suspension agent are generally any one or more of Group I and/or Group II metal compounds (CAS version of the Periodic Table of the Elements). The Group I metals of the metal compound include alkali metals (sodium, potassium, lithium, etc.) as well as Group IB metals such as copper. The preferred Group I metals are sodium, potassium, and lithium, more preferably sodium and potassium, and most preferably sodium. The Group II metals include the alkaline earth metals (magnesium, calcium, barium, etc.) as well as the Group IIB metals such as zinc or cadmium. The preferred Group II metals are magnesium, calcium, barium, or zinc, more preferably magnesium or calcium, and most preferably calcium. Generally the metal compounds are admixed into the film forming lubricant composition as metal salts, and are preferably metal bases. In one embodiment at least half of the equivalents of the suspension agent are Group II salts. In a preferred embodiment at least half, preferably at least 80%, by weight of suspension agent is an alkaline earth metal compound, e.g., calcium. In each of the above embodiments, the anionic portion of the salt can be any counterion, e.g., a hydroxyl, oxide, carbonyl, carbonate, borate, nitrate, etc. Preferably the anionic portion is a base, e.g., a hydroxyl, a carbonyl, a carbonate, or mixture thereof. In a preferred embodiment, the suspension agent comprises metal-base salts in an amount such that the basic equivalents of base anions are at least 1.5 times the acidic equivalents of film forming liquid lubricant.

[0054] Alternately or additionally, the suspension agent can comprise or consist essentially of one or more liquid coating amines. Representative liquid coating amines are described in for example U.S. Patent 5,320,768, the disclosure of which is incorporated herein by reference thereto, describing

an amine is represented by the formula R_1-N-$(R)_2$, where each R group is a C2 to C5 alkylene and the R1 group is a C3 to C24 saturated or unsaturated aliphatic group or two saturated or unsaturated aliphatic group with an oxygen therebetween, wherein the amine has between ten and thirty carbon atoms. Another useful liquid coating amine is a basic amine compound of marked oleophilic nature and at most limited water solubility, which is capable of forming salts with carboxylic acids, as disclosed in U. S. Patent 5,348,938, the disclosure of which is incorporated herein by reference thereto. In particular, optionally olefin-unsaturated aliphatic, cycloaliphatic and/or heterocyclic oleophilic basic amine compounds which contain one or more N-groups capable of forming salts with carboxylic acids are included, for example a basic amine compound having at least one long-chain hydrocarbon radical with 10 to 24 carbon atoms, which can be olefin mono- or poly-unsaturated. The filming amine can be a corrosion inhibitor which plates out or coats metal surfaces, such as Arcor 233 available from Baker Performance Chemicals, Dayton, Tex.

[0055] If the composition is substantially free of metal salt suspension agents, it is preferred that the moles of amine are at least 1.5 times, more preferably at least 2 times, the moles of tall fatty acids in the liquid film forming lubricant.

[0056] In preferred embodiments of the invention, where liquid coating amines are included in the suspension agent, the suspension agent further comprises metal-base salts in an amount such that the basic equivalents of base anions are at least 1.5 times the acidic equivalents of film forming liquid lubricant.

[0057] The film forming agent and the suspension agent can be reacted to form a grease as is known in the art. The film-forming lubricant and the suspension agent should be present in an amount to give an over-based composition. Over-basing, also referred to as superbasing or hyperbasing, is a means for supplying a large quantity of basic material in a form which is soluble or dispersible in the fatty acid. Overbased products have been long used in lubricant technology to provide detergent additives. Overbased materials are often single phase, homogeneous systems characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt, e.g., a composition having about 12 parts calcium hydroxide per 88 parts of linoleic acid, by weight, has a metal ratio of one. A composition having 1.5 times as much metal as present in a neutral salt will

have a ratio of 1.5. For example, a composition having 14 parts calcium hydroxide per 86 parts of linoleic acid, by weight, will have a metal ratio of about 1.2. A composition having about 17 parts calcium hydroxide per 83 parts of linoleic acid, by weight, has a metal ratio of 1.5. It is preferred that the metal ratio of the suspension agent to film forming liquid lubricant is greater than about 1.2. The ratio of equivalents of suspension agent to film forming liquid lubricant of the present invention in one embodiment has a metal ratio of greater than 1.5, e.g., from 2 to 12, for example 3 to 6 or alternatively 3.5 to 5.

[0058] Promoters are chemicals which are sometimes employed to facilitate the incorporation of suspension agent metal into the basic metal compositions. Among the chemicals useful as promoters are water, ammonium hydroxide, organic acids of up to about 8 carbon atoms, nitric acid, hydrochloric acid, metal complexing agents such as alkyl salicylaldoxime, and alkali metal hydroxides such as lithium hydroxide, sodium hydroxide and potassium hydroxide, and mono- and polyhydric alcohols of up to about 30 carbon atoms. Examples of the alcohols include methanol, ethanol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, dodecanol, behenyl alcohol, ethylene glycol, monomethylether of ethylene glycol, hexamethylene glycol, glycerol, pentaerythritol, benzyl alcohol, phenylethyl alcohol, aminoethanol, cinnamyl alcohol, allyl alcohol, and the like. Especially useful are the monohydric alcohols having up to about 10 carbon atoms and mixtures of methanol with higher monohydric alcohols. It is characteristic of promoters that they are normally employed in low quantities, normally at less than 1-2% by weight of the reaction mixture for promoters which are not later removed. Thus they do not normally constitute an appreciable portion of the acid functionality of the composition, but serve rather a role more as a catalyst for the overbasing process.

[0059] The lubricant composition advantageously comprises, per barrel of lubricant composition, between 10 and about 35 pounds per barrel ("ppb"), preferably between about 15 to about 20 ppb, of a polymeric particulate mechanical lubricant. The particulate mechanical lubricant is beneficially a polymeric solid preformed into discrete particles (beads). The size of the beads can vary over a substantial range such as from 10 to 800 mesh (Tyler standard screen size), for example from 20 to 400 mesh. A preferred particulate size for the polymeric beads is 40 mesh to 100 mesh, and more preferably is 60 mesh to 80 mesh. In a preferred embodiment, the particles or beads have a weight average particle diameter between about 220 and about 280 microns, with less than 30% by weight having a diameter less than 150 microns and less than 5% by weight greater than about 350 microns. Over-sized particles can plug close tolerances found in some coiled tubing applications, while too

small a particle provides insufficient material between a tubing or drilling pipe and an annulus, for example, to adequately lubricate the tubing or drilling pipe.

[0060] In one embodiment the particulate mechanical lubricant comprises beads of one or more of crosslinked polymers, *e.g.*, polymers of styrenes, PVC/vinylacetate, vinylidene chloride/acrylonitrile, methylmethacrylate and ethylacrylate, and styrene and divinylbenzene copolymers, as disclosed for example in U.S. Patents 4,063,603; 4,172,031; 4,269,279; 4,384,095 and 4,427,793, the disclosures of which are incorporated by reference. A preferred particulate mechanical lubricant is beads formed of polymerized divinyl benzene, styrene, divinyl benzene/styrene, polystyrene crosslinked with divinyl benzene, or mixtures or combinations thereof. In a preferred embodiment the first copolymer compound comprises Lubra-Glide® Beads CE copolymer, having a specific gravity of about 1.06 to about 1.1, which are commercially available from Sun Drilling Products, Inc. Other copolymer lead products are those disclosed in co-owned U.S. Patent No. 6,541,599 and 6,348,629 the disclosure of which is incorporated herein by reference.

[0061] The components should be blended to form a substantially homogenous lubricant composition, e.g., a lubricant composition where miscible components are well mixed and where immiscible solid components are substantially evenly distributed in the lubricant composition.

[0062] The lubricant composition is particularly useful in oil well operations, including drilling, running tubing or pipe, and other activities where extreme pressures can be generated. The lubricant composition can be applied by for example admixing between 1% and 5%, for example between about 2% and 4% by volume, into drilling mud. The lubricant composition will plate out from the mud onto the metal surfaces, in strong preference to un-desired plating out for example on clay, weighting agents, and sand. The greasy fraction will hold the particulate lubricants in place.

[0063] Minor amounts of biocides may be added to the lubricant composition if appropriate for the end use.

[0064] The lubricant composition should be ecologically acceptable and accordingly in the preferred embodiment should have no aromatic constituents and no environmentally detrimental metals. A composition comprising tall fatty acids, calcium hydroxide, and polystyrene-divinylbenzene beeads has an LC50 above 750000 ppm at 2% by volume in "generic 7 mud". The concentration of the chemical in air that kills 50% of test animals in a given time (usually four hours) is the LC50 value, and the appropriate tests for various systems are known to those of skill in the art.

[0065] The lubricant has a boiling point of about 250°F to 450°F, for example, 400-450. Preferred embodiments of the lubricant composition are thermally stable and useful at downhole temperatures above 250°F.

[0066] Example

[0067] An aqueous lubricant having about 65% by volume of EZESlide™, a tall oil fatty acid compound marketed by Sun Drilling Products, Inc, about 33% by volume of calcium hydroxide, and about about 2% by volume LUBRAGLIDE CE Copolymer™ beads was blended to form an overbased, substantially uniform composition. This material was found to have an LC50 above 750000 ppm at 2% by volume in generic 7 mud. This material was added in an amount between about 2% to 3% into a drilling mud, and the lubricant composition provided excellent improvements in lubricity down-hole as exhibited by reduced torque.

[0068] As used herein, unless otherwise specifically described, the mention of a single component, for example the term "film forming lubricant", encompasses both a singular compound and a plurality of compounds that each meet the requirements of the definition of the term.

[0200] Although the present invention is described with reference to certain preferred embodiments, it is apparent that modification and variations thereof may be made by those skilled in the art without departing from the spirit and scope of this invention as defined by the appended claims. In particular, it will be clear to those skilled in the art that the present invention may be embodied in other specific forms, structures, arrangements, proportions, and with other elements, materials, and components, without departing from the spirit or essential characteristics thereof. One skilled in the art will appreciate that the invention may be used with many modifications of materials, methods, and components otherwise used in the practice of the invention, which are particularly adapted to specific substrates and operative requirements without departing from the principles of the present invention. The presently disclosed embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and not limited to the foregoing description.